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Biomass as Raw Material for Production of High-Value Products

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Abstract

Industrial production of a wide range of value-added products heavily relies on fossil resources. Lignocellulosic biomass materials are receiving increased attention as a renewable, economical, and abundant alternative to fossil resources for the production of various value-added products. Biomass feedstocks utilized for these productions include energy crops, agricultural biomass residues, forest biomass, and food-based biomass wastes. Various conversion technologies are used for production value-added products from biomass. Efficiencies of conversion technologies highly depend on the types of biomass used as raw materials that differ in contents and compositions of cellulose, hemicellulose, and lignin structures in biomass. In some conversion technologies, such as chemical, biochemical, and hydrothermal conversion techniques, biomass materials must be first broken down into smaller molecular weight components (e.g., oligosaccharides and monosaccharides) in order to be efficiently converted into target products. In this matter, pretreatment and hydrolysis play critical roles on the yield of the product(s). The chapter describes lignocellulosic materials that are used for production of top value-added products and conversion technologies to produce products in high yields. Future developments in the conversion of lignocellulosic biomass into value-added products are directly correlated to improvements of conversion technologies and selection the right types of biomass in the process.

Keywords: biomass types, value-added products, biofuels, bioproducts, conversion methods

1. Introduction

Being a nonedible portion of the plant, lignocellulosic biomass materials are attractively growing the attention as sustainable and renewable energy sources. Biomass materials can be

used for producing a wide range of value-added products, including biofuels (ethanol, hydrogen, etc.), bioproducts products (sugar and sugar alcohols, etc.), and industrially important chemicals (e.g., solvents) [1]. Conversion can be performed using a variety of methods, including chemical, biochemical, and thermochemical processes. Each method offers several advantages or disadvantages for high yielding of a certain product.

Biomass can be derived from forestry wastes such as residues of the trees and shrubs, energy crops like sorghum, miscanthus, kenaf, switchgrass, corn, sugarcane, and any agricultural residues such as corn stovers, wheat straw, etc. The diversity in the chemical composition of biomass (cellulose, hemicellulose, and lignin constituents) can affect the conversion technologies employed for production of high-value products.

2. Top value-added products from biomass

2.1. Biofuels

Ethanol is a renewable fuel made from corn, sugarcane, sweet sorghum, and other variety of carbohydrate containing sources. In the United States, the ethanol fuel industry is largely based on corn. The production consists of the fermentation of sugars to produce a dilute alcohol solution, which is followed by distillation and dehydration to produce fuel-grade ethanol. Ethanol is blended with gasoline in various amounts for use in vehicles (E10, E15, and E85). It was reported that the use of 10% ethanol (E10) blends decreases greenhouse gas emissions by 12–19% compared to petroleum-based fuels [2].

Butanol is also a biomass-based renewable fuel that can be produced by alcoholic fermentation of biomass feedstocks [3]. Butanol is commonly produced using fossil fuels, but it can also be produced from biomass. Butanol can blend with gasoline better than ethanol since it has longer hydrocarbon chain thus, has lower polarity. Butanol has an energy density similar to that of gasoline [4]. However, because of limitations and difficulties in its production it is not considered a viable biofuels like ethanol. Biobutanol is produced by ABE (acetone-butanol-ethanol) fermentation process using various substrates. ABE fermentation suffers from limitations and difficulties including low butanol titer, low butanol yield, high substrate cost (grain and molasses), end-product inhibition, and high product recovery cost by distillation [5].

Methanol is another alcoholic fuel that has a high octane rating, easily distributable, and has low volatility. Methanol has chemical and physical fuel properties similar to ethanol. Methanol is mostly produced by the catalytic conversion of syngas from fossil sources but it can be also produced from lignocellulosic biomass materials [6]. Methanol can be used directly as fuel or fuel in fuel cells or as a feedstock for the gasoline additive methyl tertiary butyl ether.

Biodiesel is another most widely used liquid biofuel; however, its production does not rely on lignocellulosic fraction of biomass. Biodiesel is produced from vegetable oil or animal fat with an alcohol and a catalyst through transesterification reaction.

Producer gas is the mixture of gases produced by the gasification of biomass materials. It is composed of CO, H₂, CO₂, and low molecular weight hydrocarbons such as CH₄. Producer gas

can be utilized as a fuel gas for heat or for electricity generation [7]. *Syngas* (synthesis gas) is a mixture of CO and H₂. Syngas has the ability to replace natural gas as a more thermally efficient liquid fuel. Electricity can be generated from the power provided by the combustion of syngas. It can also be used as a fuel source or as an intermediate for the production of other chemicals [8, 9].

Hydrogen is considered as a promising gas fuel. Hydrogen has the highest specific energy content of all conventional fuels. Its main use as fuel is in fuel cells. Fuel cells are being considered an attractive option for power generation, because of their high efficiency with no pollution [10]. Its only waste or byproduct is pure water, while hydrocarbon fuels produce massive amounts of carbon dioxide, a greenhouse gas. The development of less expensive and convenient methods for hydrogen production is a challenging issue that limits its use. Among other various conversion methods, aqueous-phase reforming (APR) technique is a promising method for high-yielding hydrogen gas production [11, 12].

2.2. Bioproducts and industrially important chemicals

Nonedible lignocellulosic biomass materials are attracting increasing attention as renewable, economical, and abundant resources to reduce dependency on petroleum resources and minimize energy and material feedstock costs. In addition to energy and fuels, biomass can be used to create valuable carbon-based chemicals and materials, known as bioproducts. These products are sugars and sugar alcohols, glycerine, furfurals, cellulose fiber and derivatives, carbonaceous materials, resins, bioplastics, etc.

Activated carbons have been used for many applications including wastewater treatment (as adsorbent and filter) [13], catalyst [14], catalyst support [15], storage material [16], etc., and can be prepared from lignocellulosic biomass. *Mesoporous carbons* play important roles as catalysts supports as well as adsorbents, membranes, supercapacitors, chemical sensors, etc. [17, 18]. Mesoporous carbons can be prepared from lignin and enhance its mesoporosity by physical and chemical activation methods.

Furfural is a natural precursor to furan-based chemicals. It has been considered an important building block for the production of nonpetroleum-derived chemicals, a new generation of bioplastics, and potential biofuels or fuel additives. Furfural and its derivatives have been used to make jet and diesel fuel range alkanes, to serve as gasoline blend stock, and to develop a new generation of biofuels and bioplastics [19, 20].

Sugar alcohols are important products in the food industry. For instance, xylitol is a pentose sugar alcohol used as a sugar substitute in the food industry because of its low caloric and anticarcinogenic properties [21]. In addition, xylitol is a building block for a variety of commodity chemicals.

Addition to sugar alcohols, following C5 and C6 sugar-derived *platform chemicals* can be transformed into new families of useful molecules: 1,4-diacids (succinic acid, fumaric acid, and malic acid), 2,5-furan dicarboxylic acid, 3-hydroxy propionic acid, aspartic acid, glucaric acid, glutamic acid, itaconic acid, levulinic acid, 3-hydroxybutyrolactone, and glycerol [22].

Biomass feedstocks are converted into plenty of *other intermediate platforms, building blocks, secondary chemicals, and products* that are used in industry, transportation, textiles, food supply, environment, housing, etc. For instance, 1,3-butadiene is the building block for the production of rubbers, which are used in the production of tires for light vehicles. Ethyl lactate is a biodegradable solvent produced by the esterification of ethanol and lactic acid, which are produced from biomass. It is used in industrial applications to replace volatile organic petroleum-derived compounds. Lactic acid, which is mostly produced by microbial fermentation of carbohydrates, is used in many applications, including in food, pharmaceuticals, polymers, etc. Succinic acid, which is a dicarboxylic acid, is precursor for the synthesis of high-value products such as commodity chemicals, polymers, surfactants, and solvents.

Lignocellulosic biomass-based *polymers* have been considered as good candidates for sustainable development as well as ecofriendly environment. A wide range of polymers can be prepared from biomass-derivatives by different reaction routes [22]. For instance, C5 and C6 sugars and their derivatives can be either incorporated in polymer backbone or be used as pendant groups to prepare glycopolymers that mimics structural and functional responsibilities of glycoproteins [23].

3. Parameters affecting the product yield

3.1. Pretreatments

Despite their potential, the complex and rigid structures of biomass materials limit their use in many applications. Biomass materials must first be broken down into components with smaller molecular weights (e.g., oligosaccharides and monosaccharides) in order to be efficiently converted into a range of products. The goal of pretreatment is to make the cellulose accessible to breakdown process (hydrolysis) for conversion to fuels or value-added products. Various pretreatment techniques change the physical and chemical structure of lignocellulosic biomass and improve hydrolysis rates. Pretreatment makes biomass accessible to deconstruction by altering structural features of biomass such as removing lignin and reducing cellulose crystallinity, thereby increasing porosity. Successful production of biofuels and other bioproducts from lignocellulosic biomass depends on the pretreatment and deconstruction methods applied as well as the physical and chemical properties of the biomass. An efficient pretreatment method followed by solubilization in aqueous media without using toxic and hazardous chemicals is necessary to obtain reduced molecular weight of carbohydrates from biomass to produce various biofuels and bioproducts other value-added products.

In *ammonia fiber explosion* (AFEX) pretreatment method, liquid ammonia is mixed with biomass under moderate pressure (0.7–2.8 MPa) and temperature (70–200°C) before rapidly releasing the pressure. The temperature of the reaction, residence time, and ammonia concentration are main parameters that affect the dissolution [24]. The sudden release of pressure in the system explosively ruptures the biomass fibers and eventually breaks down the cellulose, hemicellulose, and lignin polymers into smaller components, and increases the size and the number of micropores in the cell wall.

Steam explosion is one of the most common and widely employed physicochemical pretreatments for lignocellulosic biomass. Biomass is treated with high-pressure (0.69–4.83 MPa) saturated steam at high temperature (160–260°C) for a short time (several seconds to a few minutes) and then the pressure is rapidly released. This treatment destroys the fibril structure and makes the materials undergo an explosive decompression [25]. After the treatment, hemicellulose is degraded, part of lignin is solubilized, and cellulose binding is reduced. Partial degradation of hemicellulose and formation of toxic compounds are the main drawbacks of steam explosion process. Toxic and/or inhibitory compounds can affect and reduce the performance of fermentations steps [26]. Substances that may act as inhibitors of microorganisms include phenolic compounds and other aromatics, aliphatic acids, furan aldehydes, inorganic ions, and bioalcohols or other fermentation products [27].

Alkali pretreatment involves the use of bases, such as sodium, potassium, calcium, and ammonium hydroxides, for pretreatment of biomass. Sodium hydroxide is the most common base used in this application. Alkali pretreatment can be carried out at ambient conditions, but pretreatment times take hours or days rather than minutes or seconds [28]. Alkali pretreatment disrupts the lignin structure, causes partial decrystallization of cellulose, removes acetyl, and the various uronic acid substitutions on hemicellulose and increases the accessibility of enzymes to cellulose and hemicellulose [29]. A neutralizing step to remove lignin and inhibitors (salts, phenolic acids, furfural, and aldehydes) is required before enzymatic hydrolysis. Compared with acid processes, alkaline processes cause less sugar degradation, and many of the caustic salts can be recovered and/or regenerated [28].

Acid pretreatment is based on mixing biomass with concentrated or diluted acids at temperatures between 130°C and 210°C. The use of concentrated acid can count as a treatment method rather than pretreatment as explained in the hydrolysis section in the detail. The most commonly used acid in the acid pretreatment is dilute sulfuric acid (H_2SO_4). Other acids such as hydrochloric acid (HCl), phosphoric acid (H_3PO_4), and nitric acid (HNO_3) can also be used. As an alternative to these inorganic acids, organic acids such as maleic acid and fumaric acid can also be used for dilute acid pretreatment [30]. The application time could take from a few minutes to hours depending on the type of acid, concentration, and temperature used in the process. This pretreatment method solubilizes hemicellulose fraction and releases monomeric sugars and soluble oligomers from the cell wall matrix into the hydrolysate. After removing hemicellulose, increase in porosity improves enzymatic digestibility. However, the sugars released from hemicellulose can be further degraded to furfural and hydroxymethyl furfural, which takes role as inhibitors in fermentation process.

Other common pretreatment methods used for biomass are *oxidative delignifications*. These methods are (a) lignin biodegradation catalyzed by the peroxidase enzyme in the presence of H_2O_2 , (b) lignin degradation caused by ozone, which attacks and cleaves aromatic ring structures, while hemicellulose and cellulose are hardly decomposed (*ozonolysis*) [25], (c) the internal lignin and hemicellulose bonds in presence of an organic are broken by using methanol, ethanol, acetone, ethylene glycol, triethylene glycol, or tetrahydrofurfuryl alcohol or aqueous organic solvent mixture in presence of inorganic acid catalysts such as HCl and H_2SO_4 or organic acid catalysts such as oxalic, acetylsalicylic, and salicylic acids (*organosolv*

process) [28], and (d) biomass is treated with oxygen or air as an oxidizer in combination with water at elevated temperature (e.g., 195°C) and pressure (e.g., 1.2 MPa) (*wet oxidation*). Wet oxidation mainly solubilizes hemicellulose and removes lignin from biomass structure. Lignin is decomposed into carbon dioxide, water, and carboxylic acids. In this method, the formation of strong inhibitors such as furfural and 5-hydroxymethylfurfural is very low.

There are also some methods that use *ultrasound, microwave, and radiofrequency radiations* as pretreatments methods. These pretreatments are used in conjunction with other methods. Ultrasound produces sonochemical and mechanoacoustic effects, which affect the chemical and physical composition of biomass. The mechanoacoustic alters the surface structure of the biomass while the sonochemical production of oxidizing radicals is effective on biomass components [31]. It was reported that sonication of biomass-water mixture under 20 kHz ± 50 Hz ultrasound for 8 min did not change the hydrolysis that was performed in subcritical water after sonication. Although hydrolyzed solid biomass fraction remained the same, the molar mass of polysaccharides fractions in the hydrolysates notably decreased because of degradation. The amount of monosaccharides in sonicated hydrolysates was high that confirming the positive effect of sonication on degradation of polysaccharides. For instance, hydrolysis of kenaf biomass at 250°C subcritical water treatment resulted in 10% of more xylose release in the sonicated hydrolysate compared to nonsonicated one [32].

On the other hand, microwave treatment has enhanced the surface disruption and the breaking of lignin structures in switchgrass and improved enzymatic saccharification 53% more compared to conventional heating [33]. Microwave pretreatment has positive effect on solubilization of switchgrass in subcritical water. Hydrolysis percentages and total organic carbons released into solution are higher in microwave-treated biomass samples. When microwave pretreatment is applied at higher temperature, solubilization significantly increases (Table 1).

Biomass ^a	Hydrolysis ^b (%)	TOC (mg L ⁻¹)
Untreated	49.01 ± 0.9	1132 ± 13
MW — 120°C	57.09 ± 0.6	1541 ± 14
MW — 150°C	62.91 ± 0.7	1679 ± 17

^aMW: microwave-treated biomass.
^bDetermined by weighing microwave-treated biomass samples before and after solubilization in subcritical water treatment.

Table 1. Solubilization of microwave pretreated samples in subcritical water.

Microwave pretreatment was used for solubilization of lignocellulosic biomass in combination with acid and alkali treatments followed by enzymatic hydrolysis [33–35]. Chimentão et al. [36] investigated hydrolysis of dilute acid-pretreated cellulose in a conventional oven and under microwave heating. Although the method was called “mild hydrothermal conditions,” the hydrolysis process was accelerated using acids (sulfuric and oxalic acids).

Radio frequency (RF) heating is another promising dielectric heating technology, which is used as an initial breakdown of the lignocellulosic matrix. Dielectric heating transforms electromagnetic energy into heat that is effective on breakdown of biomass structure. The electromagnetic field could generate nonthermal effects, which can also accelerate the destruction of the crystallinity structure [37]. RF heating prevents uncontrolled heating and overheating that protects the product from degradation. RF has large penetration depth (10–30 m) and higher energy efficiency than microwave [38–40]. Efficiency of pretreatment highly depends on temperature, frequency, and type of product/biomass (water content, chemical composition, etc.). Radio frequency-assisted dielectric heating was usually combined with alkaline pretreatment for destruction of biomass materials [41, 42].

Biological pretreatments are attractive approaches for delignification of lignocellulosic biomass. Advantages of these processes are mild operation conditions, environment friendly, and low energy requirement [43]. The formations of toxic materials (furfural, hydroxymethylfurfural, etc.) are low. However, these pretreatments are time consuming [44]. The microbial treatment includes fungi, such as white-rot fungi, brown-rot fungi, and soft-rot fungi, actinomycetes, and bacteria to degrade recalcitrant polymeric structures in biomass [45]. Brown rots are mainly effective on polysaccharides with minimal lignin degradation, whereas white and soft rots attack carbohydrates and lignin. Most of the brown-rot fungi degrade cellulose and hemicellulose more rapidly than lignin in lignocellulosic biomass. White-rot fungi are the most effective for biological pretreatment of lignocellulosic materials since they are able to efficiently degrade all components of plant cell walls, both carbohydrates and lignin. Enzymes such as peroxidases and laccase take roles on lignin degradation by white-rot fungi. Bacteria and actinomycetes are not as efficient as white- and brown-rot fungi in pretreatment of biomass. Lignocellulosic biomass materials such as wheat, corn and rice straws, corn stover, corn stalks, beech wood chips, pine wood chips, and switchgrass were successfully pretreated by these methods using white-rot fungi, brown-rot fungi, and soft-rot fungi [46–48].

Many applications have combined one pretreatment with other one for effective breakdown of biomass structure.

3.2. Hydrolysis of biomass materials

The major hydrolysis processes typically used for the solubilization of biomass require either use of toxic, corrosive, and hazardous chemicals (e.g., acid and alkali treatments) or longer retention times (e.g., enzymatic hydrolysis), which collectively make the process environmentally unsafe and/or expensive. Mineral acids are commonly used to dissolve hemicelluloses, whereas lignin is typically dissolved by alkaline or organosolv pretreatments [45, 49]. Recovery of the chemical catalyst is often crucial to the success of these processes [24]. On the other hand, generally harsh conditions (e.g., high temperatures and high acid concentrations) are needed to release glucose from biomass complex structures. Pyrolysis and other side reactions at higher temperatures become very important, and the amount of undesirable byproducts (tars) increases as the temperature is increased above 220°C [50].

Concentrated acid hydrolysis has been applied to breakdown lignocellulosic efficiently. The hydrolysis reaction for cellulose conversion into sugars is principally the degradation of

chemical bonds in cellulose, involving the hydrolytic cleavage of beta-1,4-glycosidic bond, which is catalyzed by H_3O^+ ions of an acid. The reaction rate depends on the H_3O^+ ion concentration, the reaction temperature, and the chemical environment of the glycosidic bond [51]. The acid hydrolysis process usually employs sulfuric acid and hydrochloric acid at concentrations of 1–10% using a moderate temperature (in the range of 100–150°C) [52]. A two-step sulfuric acid hydrolysis is a widely used technique for releasing sugars from biomass. Biomass is first treated with concentrated sulfuric acid at a low temperature and then hydrolyzed with diluted sulfuric acid at an elevated temperature. Concentrated acid recrystallizes cellulose to less crystallized oligosaccharides followed by less concentrated and higher reaction temperature for converting recrystallized oligosaccharides to monosaccharides. Advantages of concentrated acid hydrolysis process are higher conversion from polysaccharides to monosaccharides with minimum formation of reaction byproducts with careful control of reaction conditions. The use of concentrated acid for biomass hydrolysis has also several drawbacks such as energy consumption, equipment corrosion, handling of nonsafe chemicals, an added necessary step of acid neutralization, the formation of byproducts that create an inhibitory effect in the fermentation [53, 25], and other negative environmental impacts. On the other hand, *hydrothermal treatments* (subcritical and supercritical water) are alternative ways to hydrolyze lignocellulosic biomass in an environmentally friendly manner by only operating temperature and pressure conditions. The main shortcoming of these applications is their very high investment cost. **Figure 1** shows morphological changes occur in biomass structure (kenaf) after subcritical water hydrolysis treatment [32].

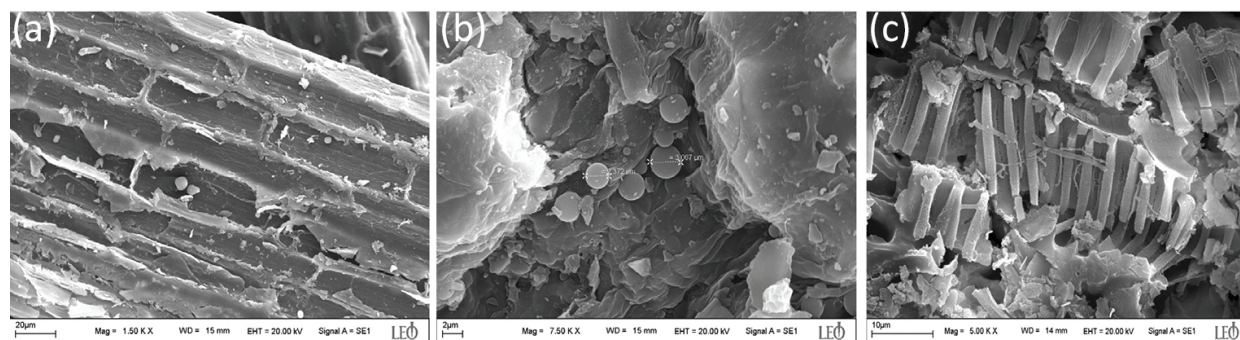


Figure 1. SEM images of untreated (a), 200°C (b) and 250°C (c) subcritical water treated kenaf samples.

Before treatment biomass exhibits rigid and highly ordered fibrils. The cell walls are visible creating a “brickwork-like” appearance to surface (a). The compacted outer layer is partially removed at 200°C and a range of discrete droplet morphologies that contain lignin is appeared on the cell. The 250°C-subcritical water treatment reduces and degrades lignocellulosic structure, leaving highly degraded solids. The maximum solubilization yield of wheat straw and kenaf biomass were found to be 70–75% in subcritical water medium (under 250°C and 27.58 MPa carbon dioxide pressure conditions) [11, 32]. However, the hydrolysates obtained in this process contained high molecular weight polysaccharides that were difficult to utilize for producing value-added products such as gas biofuel hydrogen.

3.3. Chemical composition of biomass materials

Chemical composition of biomass and structures of biopolymers (cellulose, hemicellulose, and lignin) are two important factors affecting the yield of the biofuels, bioproducts, and chemicals produced from biomass. Composition of lignin, cellulose, and hemicellulose in biomass materials significantly differ among biomass species. For instance, some biomass materials such as hardwoods contain more cellulose in their structures, whereas others such as straws and leaves have more of hemicelluloses. It is known that lignin content of herbaceous plants such as grasses is very low compared to softwoods, which are known to have highest amount of lignin in their structures [54]. On the other hand, polymerization degree and(or) structures of biopolymers can also considerably varies among biomass species. For instance, the chemical structure of lignin is based on syringyl (S), guaiacyl (G), and p-hydroxyphenyl (H) units. Softwood lignins are mainly composed of residues derived from guaiacyl units (lignin type G), whereas hardwood lignins contain both syringyl and guaiacyl units with minor amount of p-hydroxyphenyl (lignin type GS). Lignins from grasses are composed of the three basic precursors (lignin type HGS) [55, 56]. Hemicellulose fractions of softwoods mainly have D-mannose-derived structures such as galactoglucomannans, whereas hemicelluloses in hardwoods have D-xylose-derived structures such as arabinoglucuronoxylan. Xylan is a polypentose hemicellulose structure in biomass materials that displays a wide range of compositions, molecular sizes, and structures depending upon its source [57, 58]. This diversity among biomass materials can significantly affect the yield of value-added products directly produced from biomass as raw materials. On the other hand, this diversity can also affect solubilization efficiency of the biomass materials and, therefore, contents and compositions of the biomass components in the hydrolysates. The differences in the hydrolysates will considerably change the yield of the target compounds and byproducts produced from these biomass hydrolysates. For instance, molecular weight distribution of carbohydrates in the hydrolysates can significantly affect the method employed for biofuel or useful chemicals production. The more degraded organics containing hydrolysates are preferable for the production of certain various value-added products from biomass. For example, high-yielding hydrogen gas production from biomass hydrolysates requires reduced molecular weight oxygenated compounds containing biomass hydrolysates as feeds in aqueous-phase reforming gasification process [59].

3.4. Conversion methods

3.4.1. Chemical

Sugars released from biomass can be hydrogenated to C5-6 polyols (*sugar alcohols*) by using a chemical reducing agent such as sodium borohydride (NaBH_4). Biomass hydrolysates can also be utilized for direct production of derivatives, such as *furfural*, *hydroxymethyl furfural*, and/or *levulinic acid*. It is also possible to produce C2-3 *glycols* from biomass hydrolysates by hydrogenolysis. Sugar containing hydrolysates are further upgraded via oxidation or halogenation reactions [60]. Sugars obtained from biomass hydrolysis can be converted to N-heterocyclic

components, pyrones, and aromatics that can be further converted into a *variety of chemical intermediates*.

Furfural is a valuable compound for a variety of chemical applications and it serves as a precursor for the synthesis of many fine chemicals and biofuels. It is produced industrially by acid-catalyzed hydrolysis and dehydration of pentoses (mainly xylose) in lignocellulosic feedstocks (sugarcane bagasse, corn cobs, sunflower stalk, etc.) at temperatures ranging from 153 to 240°C [61]. During the initial stage, the hemicellulose is hydrolyzed to xylans, which generate pentose carbohydrates to be further converted into furfural. Commercially, furfural is produced using sulfuric acid as a homogeneous catalyst. Significant quantities of steam are used in the process in order to strip the furfural and to avoid its further degradation.

Xylitol is currently produced through chemical reduction of xylose derived from birch wood chips and sugarcane bagasse hemicellulose hydrolysate. The chemical process adapted for xylitol production from xylan-rich biomass demands high production costs in terms of temperature and pressure input, as well as the formation of byproducts that require expensive separation and purification steps [62].

3.4.2. Thermochemical

Thermochemical conversion processes are combustion, pyrolysis, gasification, and liquefaction.

Combustion of biomass is the least complex conversion method to transform biomass into energy. Combustion process takes place at 800–1000°C. Complete combustion involves the production of heat as a result of the oxidation of carbon and hydrogen-rich biomass to CO₂ and H₂O. The biomass with high moisture content is not suitable for this process, predrying may be necessary in some cases. The high-pressure steam formed in the process can be utilized as hot air, hot water, steam, or electricity to produce hot gases. Combustion systems for electricity and heat production are similar to most fossil-fuel fired power plants. Combustion technologies can produce high NO_x emissions.

Pyrolysis is thermal degradation of lignocellulosic biomass in the absence of oxygen around 500°C. The products are combination of solid (biochar) and gaseous fractions and liquid biooil (biocrude). These products can be used directly or after processing as fuel. Biochar and biooil can also be utilized for production of chemicals and value-added products [63]. Pyrolysis is a part of gasification and combustion, which consists of a thermal degradation of the initial solid biomass into gases and liquids without an oxidizing agent. Thermal decomposition of organic components in biomass starts at 350–550°C and goes up to 700–800°C in the absence of air/oxygen [64]. Pyrolysis can be fast or slow process depending on time taken for processing the feed into pyrolysis products. In slow pyrolysis, primarily biochar is produced at lower temperatures. At higher temperatures biooils are produced through fast pyrolysis. In slow pyrolysis, biomass is typically heated at slow heating rates (up to 10–20°C min⁻¹ with sufficient time allowed for repolymerization reactions to maximize the solid yields while fast pyrolysis uses much higher heating rates >10–200°C s⁻¹), higher processing temperature and short vapor residence times (less than 2 s) that produce 50–70 wt% biooil yield (dry biomass basis). Fast

pyrolysis usually requires a finely ground biomass feed (<1 mm); however, slow hydrolysis accepts a wide range of particle sizes (5–50 mm) [65].

Gasification is the conversion of biomass into a combustible gas mixture at 700–1600°C. The produced gas is rich in CO, H₂, CH₄, and CO₂. This combustible gas mixture can be used for different purposes after cleaning. The clean gas can be used directly as an engine fuel or upgraded to liquid fuels or converted into chemical feedstocks by different methods including biological fermentation or catalytic upgrading through the Fischer-Tropsch process [7, 19].

Lignocellulosic biomass can also be converted into liquid and gaseous fuels by *hydrothermal gasification processes*. Hydrothermal gasification processes are applied in either gaseous phase (steam reforming), in supercritical water, or in liquid phase (aqueous phase reforming). Steam reforming needs the lignocellulosic material to be dried prior to gasification. The temperatures applied in this conversion are also high, i.e., 800°C or above and considerable tar and char are formed. The thermodynamic critical points for water are 374.3°C and 221.2 bar for temperature and pressure, respectively. Effective gasification of lignocellulosics in supercritical water needs to go quite higher values than the critical points, e.g., above 600°C for complete gasification [66]. APR gasification process is a promising process since conversion reactions take place at moderate temperatures (225–265°C, and at pressures of 27–54 bar) in presence of a reforming catalyst (such as precious metal, Pt). The water-gas shift reaction ($\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{H}_2 + \text{CO}_2$) is thermodynamically favored at processing temperatures. Biomass hydrolysates, which are composed of biomass-derived mixed oxygenated hydrocarbons, are successfully converted into gaseous products that are rich in hydrogen [12, 59, 67].

Hydrothermal liquefaction of biomass is the thermochemical conversion of biomass into liquid fuels at 280–370°C and 10–25 MPa in aqueous medium [68]. In this process, water is an important reactant and catalyst. It is still in liquid state and has a range of promising properties at the liquefaction conditions [68]. In this process, lignocellulosic biomass is break down into soluble low molecular weight products that undergo further condensation, cyclization, and polymerization reactions forming biooil that is soluble in organic solvents. These biooils are most commonly used as a replacement for petroleum fuels but they can be also served as feedstock for production of a wide range of value-added products. For instance, lignin-derived phenolics can be converted into aromatic chemicals by hydrogenation [69], and carbohydrates are utilized for catalytic production of hydrogen or consumed in fermentation [70].

Various value-added products can be produced or synthesis from biomass or biomass-derived compounds by thermochemical methods. For instance, sugars can be reduced into sugar alcohols by thermochemical reduction. In industrial reaction, sorbitol production by thermochemical reduction of glucose is mainly carried out discontinuously in stirred tank reactors at 100–180°C under 5–15 MPa of H₂ pressure in the presence of a catalyst, usually raney-type nickel, or ruthenium catalysts. **Table 2** shows thermochemical sugar alcohol production from glucose, simple biomass model compound, at various processing temperatures under 2.0 MPa H₂ pressure in the presence of carbon supported ruthenium catalyst. The reaction time was 60 min [71].

The results showed that 80°C hydrogenation temperature is not enough for complete reduction of glucose solution. Further increase of the process temperature causes complete reduction of all glucose; however, the contents and compositions of reduced products (sugar alcohols) significantly change as temperature increased. The main reduction product of glucose is sorbitol and its highest yield is at 100°C at the processing conditions described above.

Temperature (°C)	Sugar alcohols (% concentration)				
	Glucose	Mannitol	Sorbitol	Xylitol	Other products ^b
80	8.8	0.9	90.3	n.d.	n.d.
100	n.d. ^a	2.2	97.3	n.d.	n.d.
120	n.d.	5.9	88.6	n.d.	5.5
140	n.d.	16.5	59.7	2.7	21.1
160	n.d.	21.8	41.0	3.6	33.6
180	n.d.	23.4	20.7	4.1	51.8
200	n.d.	19.7	12.1	2.1	66.1

^an.d., not detected.

^bTotal of other reduced products (glycerol, erythritol, etc.).

Table 2. Thermochemical sugar alcohol production from reduction of glucose at various temperatures.

Other types of value-added products that can be produced by a thermochemical method are carbonaceous materials. Nonsolubilized residue containing mostly lignin and lignin destruction products can be utilized for production of carbon-based materials such as activated carbon and mesoporous carbons, etc. [72].

3.4.3. Biochemical

Biochemical conversion can also be used for breaking down biomass into sugars that can then be converted into biofuels (gaseous or liquid fuels) and bioproducts through the use of microorganisms and enzymes. This process is usually used for treating high moisture containing organic wastes. Biochemical processes are relatively slow processes that require more time for conversion of biomass into useful compounds [73]. The most popular biochemical technologies are *anaerobic digestion* and *fermentation* [74]. Biomass from various sources is biochemically degraded by *anaerobic digestion* in highly controlled, oxygen-free condition circumstances to produce biogas containing mostly methane and carbon dioxide. Biogas can be burned directly for heat or steam or converted to electricity. It can also be upgraded to biomethane or reformed into hydrogen fuel. In anaerobic digestion, bacteria are used to hydrolyze carbohydrates into sugars that are digestible by other bacteria. Methane and carbon dioxide are produced from those digestible components.

Fermentation is used commercially on a large scale to produce ethanol from carbohydrate containing materials. Structural carbohydrates in biomass are broken down into sugars by

using enzymes. Then, released sugars are transformed into alcohols, organic acids, or hydrocarbons by microorganisms in fermentation. The intermediate sugars can also be utilized to obtain other value-added chemicals. Conversions in this process take place at 25–70°C under atmospheric pressure conditions.

Not only biofuels but also a wide range of value-added products such as food-based sugar alcohols (e.g., xylitol) can be produced by combined processes such as thermochemical process combined with a chemical or biochemical method [62].

4. Comparison of various types of biomass materials for high-yielding value-added products

4.1. Energy crops

Energy crops are specifically grown for its fuel value or to produce bioenergy. These plants usually require low cost and low maintenance to grow and they are utilized to make biofuels or directly exploited for their energy contents. Energy crops can be food crops (corn, sugarcane, sugar beet, sweet sorghum, etc.) or nonfood crops (poplar trees, switchgrass, miscanthus, kenaf, etc.). A major focus among them is nonfood energy crops.

Perennial grasses (C4 species) such as switchgrass and miscanthus are promising potential lignocellulosic biomass sources for biofuel production. They require less fertilizer, water, and energy for production. Since these grasses regrow from their roots, they do not need to be replanted each year. Switchgrass and miscanthus are being developed as bioenergy crops because they have high yield potential and desirable agronomic traits. Switchgrass is a native prairie plant that grows about 10 feet tall. Annual dry matter yields are 15–30 t ha⁻¹. It exhibits adaptation to relatively wet and fertile soils. Switchgrass is very tolerant of poor soils, flooding, and drought. It greatly reduces soil erosion. Giant miscanthus is a perennial warm-season (C4) sterile hybrid grass. It is native to subtropical and tropical regions of Africa and southern Asia, which has also been used as an ornamental plant in many countries. Giant miscanthus can grow best in the soils that are well drained and have a pH between 5.5 and 7.5 under medium to high fertility [75]. Giant miscanthus has produced more than double the biomass of upland switchgrass per acre. Yield estimates from 10–15 tons per acre. Harvestable stems of miscanthus are usually more than 9 feet long [76].

Kenaf (Hibiscus cannabinus L.), is a warm season annual herbaceous crop that belongs to Malvaceae family and grows best in the tropics and subtropics where the mean daily temperatures during the growing season exceed 20°C. Kenaf is a good candidate for bioenergy because it grows fast without special care and produces large amount of biomass. Under good conditions, kenaf will grow to a height of 5–6 m in 6–8 months and produce up to 30 t ha⁻¹ y⁻¹ of dry stem material [77].

Corn is one of the most important crops in the world, and the United States is the largest corn producer in the world. The total production of corn in the United States for the year 2014–2015 was reported to be 14.215 billion bushels [78]. A major use of corn in the United States is ethanol production (30.5%). Other uses beyond animal feed include the production of high fructose corn

syrup (3.6%), sweeteners (2.1%), starch (1.8%), cereals (1.5%), beverage alcohol (1.0%), etc. [78]. The amount of cropland devoted to growing corn has considerably increased in recent years and now, the United States has excess corn production. Ethanol production capacity from corn has reached about 15.25 billion gallons in 2014/15, exceeding projected capacity demand of 15.1 billion gallons per year [79]. Most ethanol in the United States is made from corn because it is a relatively low-cost source of starch that can easily be converted into sugar, fermented, and distilled into ethanol. Today, more than 10% of vehicle fuel comes from ethanol. Producing ethanol increases the cost of corn, which leads to *higher* prices for other commodities such as dairy, meat, and livestock feed that farmers rely on. Since ethanol use has increased incredibly since 2000, the demand and the price of corn have increased. This has forced the farmers to use more pristine lands to plant corn. This land conversion and the associated use of agricultural fertilizers and pesticides have caused significant increases in greenhouse gas emissions. Even more emissions were released when ethanol consumed as fuels. Because ethanol has less energy content than gasoline, vehicles have to consume more fuel and thus produce more emissions.

Sugarcane (*Saccharum* spp.) is an efficient tropical/subtropical grass with nitrogen-fixing symbionts, thus needing little fertilizer. Brazil is the largest producer (31 million tons year⁻¹) and produces 25% of the world's sugarcane [80]. Commercial average of sugar cane yield (Australia, Colombia, and South Africa) and total dry matter (biomass) production are reported to be 84 and 39 t ha⁻¹ yr⁻¹, respectively [81]. A cycle of sugarcane planting and harvesting is about 12 months. The average sugarcane yield from four cycles is about 60 t ha⁻¹ yr⁻¹ [82]. The sugarcane industry's waste product, bagasse, can also be used to produce biofuels. Bagasse is the fibrous residue left over when sugarcane is squeezed for its juice. It was reported that energy balance of sugarcane-based ethanol is seven times greater than that of corn-based ethanol. Energy balance defined as the difference between the energy consumed to produce ethanol from crop and the energy released when it is consumed as biofuel. Only certain percent of corn starch can be converted into ethanol that required an initial breakdown process to release sugars from starch first. This step significantly increases the operation costs compared to sugar-based ethanol [83].

Poplar trees are already known to be good candidates for bioenergy because of their fast growth rates (up to 4 m annually and matures in about 6 years) and large biomass production. Poplar can grow on 2–3 year rotations, growing back after it is harvested, with seven or more cycles possible before replanting. After harvest, the tree resprouts from the same root stalk, a very efficient way to produce biomass. Hybrid poplars have been planted for their potential as an energy crop due to their high yield rates and adaptability to many growing conditions. Hybrid poplar growth and biomass yield could vary significantly depending on climatic conditions, soil characteristics, and species genotype [84, 85]. Poplar plantations have many environmentally desirable applications, including use as buffer strips to decrease erosion and nitrate in run-off from highly erodible fields, treatment, and removal of toxic materials from landfills and other soil contaminations, and an excellent sink of atmospheric CO₂ [86]. Poplar woods do not need to be stored like other bioenergy crops such as grasses; it can be harvested throughout the year. Poplar requires less water and other inputs than crops such as corn. The

higher pest resistance, increased site adaptability, and development of poplar genotypes with improved yield make poplar trees important biomass materials for biofuel production.

Sweet sorghum (*Sorghum bicolor* L. Moench) is a widely adapted sugar crop that can be produced at less cost than corn [87]. It is a highly productive and versatile crop that can be cultivated in temperate climates. Sweet sorghum can be grown in many regions of the United States. Under favorable growing conditions, sorghum can produce high biomass yields with low rates of nitrogen fertilizer. Individual stalks can be over 10 feet tall. Two fractions of sweet sorghum can be used for biofuel production. The stalk and seed are used directly for biomass energy, and their high sugar content allows them to be fermented to make ethanol. Rather than producing starch, sweet sorghum carbohydrates are stored in the stalk as sugar, with sugar concentrations of 8–20% [88]. As the plant matures, carbohydrates are translocated from the stalks to the head to make starch in the seeds. Conversion of these sugar components into ethanol requires less energy than starch for same reason discussed for sugarcane. Sweet sorghum has the potential to produce up to 6000 L ha⁻¹ of ethanol equivalent to corn grain yields of approximately 20 Mg ha⁻¹ [89]. The main drawback in sweet sorghum is; since sugars in the sweet sorghum are not stable and rapidly degrade it is required to squeeze the juice out immediately for conversion. This reduces flexibility in harvesting and can increase transportation costs [90].

4.2. Agricultural biomass residues

Agricultural residues from well-established production chains are important sources of biomass that can provide a substantial amount of biomass for production of a wide range of value-added products. Since these residues are a natural byproduct of the food crop, they can be used as promising low-cost feedstocks without increasing the amount of land used for agriculture. Agricultural biomass includes *bagasse, straw, stem, stalk, leaves, husk, shell, peel, pulp, stubble*, etc. is produced annually worldwide and is not utilized to any significant extent.

Cereal straw is a typical example of an agriculture byproduct. Rice straw (includes stems, leaf blades, leaf sheaths, and the remains of the panicle after threshing) and wheat straw (includes nongrain portion of the wheat plant; stems, leaves, and chaff) are two of the most abundant cereal-based lignocellulosic wastes in the world. Wheat is the second most important grain that is cultivated in the United States, following only corn. The United States is a major wheat-producing country ranked third in production volume of wheat in the world. Total wheat production in United States was about 55 million tons in 2015. A good wheat crop yields between 1 and 1.2 tons of straw per acre on a dry matter basis. The annual global rice straw production is 731 million tons and Asia alone produces 667.6 million tons [1]. One ton of rice paddy produces approximately 290 kg rice straw. Rice husk is one of the major byproducts from the rice milling process and constitutes about 20% of paddy by weight. One ton of rice paddy produces roughly 220 kg rice husk [2].

High-yielding corn production activities generate large amounts of corn stover that is roughly 80% of all agricultural residues produced in the United States [91]. It has been estimated that corn in the United States produces 1.7 times more residue than other cereals. Corn stover contains 27.5% stalk, 8.2% cob, and 7.0% husk [92].

Biomass	Advantages and disadvantages
Switchgrass and miscanthus	Nonedible Require less fertilizer, water, and energy for production Do not need to be replanted each year Miscanthus produces more biomass than switchgrass
Kenaf	Nonedible Grows fast in the tropics and subtropics Does not need special care for production produces large amount of biomass
Corn	Edible Mostly used for ethanol production because of relatively low-cost source of starch Large amount of cropland devoted to corn Excess corn production in the United States
Sugarcane	Edible Grows in tropics and subtropics Needs little fertilizer Sugarcane juice is directly used in conversion techniques (no pretreatment needed) Waste product, bagasse, is an important feedstock for value-added products
Sweet sorghum	Needs little fertilizer Sugars in the juice can be directly utilized for value-added products (no pretreatment needed) Required to squeeze the juice out immediately (not stable) Limited flexibility in harvesting and transportation costs
Poplar trees	Nonedible Grow fast Produce large amount of biomass Can be harvested throughout the year Have many environmentally desirable applications such as reducing erosion
Cereal straw	Nonedible Natural byproduct of the food crops rice, wheat, corn, etc. Produce large amounts of biomass
Corn stover	Nonedible Natural byproduct of the food crop, corn Produce large amounts of biomass (more than cereals)
Forest biomass	Nonedible Largest source of lignocellulosic biomass High costs of harvesting and transportation Widely used in combustion process but not in gasification, pyrolysis, and fermentation
Food biomass wastes	Edible/nonedible Have low values Released in large amounts from food industries

Table 3. Comparison of biomass materials for production of value-added products.

4.3. Forest biomass

Forests are the largest source of lignocellulosic biomass that can be substitute for fossil fuels in the production of energy and other value-added products. Since it is a nonfood type of biomass, it is a promising feedstock for these conversions [93]. Forest biomass includes material left on logging sites (*trunks, crowns, and branches*), *unused wood* from forests and *wood manufacturing, and processing residues*. The wastes from wood industries are sawdust, off-cuts, trims, and shavings. Forest biomass utilization has some challenges that restrict fully production of value-added products from forests. The main issue is high costs of harvesting and transportation of these biomass materials. Second, forest biomass has been widely used in combustion process, however, other potential conversion technologies such as gasification, pyrolysis, and fermentation are not applied to forest biomass [94].

4.4. Food biomass wastes

The food industry produces a large number of residues and byproducts that can be used as biomass energy sources.

Bagasse is a promising biomass material that is produced during sugarcane processing. After sugarcane is milled for juice extraction, bagasse is obtained as a residue, which is about 25% of the total weight and contains 60–80% carbohydrates [95].

Pomace is also important food waste-based biomass candidate from wine industry that remains after the grapes are pressed and consists of skins, seeds, and a small percentage of stems. It is the most abundant wine-making waste representing about the 20% (w/w) of grapes used for the production of wine. It is rich in carbohydrates [96].

Nuts hulls, peanuts shells, corn stover, rice hull/husk, and other grain biomass residues can also be considered food biomass wastes. On the other hand, *corn bran*, a byproduct of the corn milling process, can also be counted as lignocellulosic biomass. A large starch producer in the United States releases approximately 9×10^5 tons of corn bran per year [97]. However, this byproduct currently has low value and is often used for animal feed alone or combined with corn germ cake or meal.

Table 3 summarizes advantages and disadvantages of biomass materials for utilization as raw materials for production of value-added products.

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